Plating Plastics with Electroless Nickel In a Bath Containing Boron Hydride Hydrazine

By W. Rekść and A. Idziak

A nearly neutral electroless nickel bath containing sodium acetate, boron hydride hydrazine as the reducing agent and sodium thiosulfate as the stabilizing agent can be operated at 30 to 35° C to produce semibright deposits with satisfactory adherence on etched, sensitized and activated ABS substrates. The efficiency was 57.5 percent when the bath was operated with optimum conditions.

Metallized plastics have been adopted by many industries because of their decorative features, improved mechanical strength and good corrosion resistance. Before they are electroplated, plastics are chemically metallized with copper or nickel to make them electrically conductive.[1-3]

For the chemical deposition step in a decorative plating process, nickel is more popular than copper because nickel can be directly electroplated with bright nickel. The complete process becomes less time consuming because copper plating is omitted. Furthermore, corrosion resistance is improved and the nickel exhibits better adherence to the plastic.

Sodium hypophosphite has been the most popular reducing agent for electroless nickel plating.[1-3] Another reducing agent is sodium borohydride, but this compound must be used exclusively in a strong alkaline solution at temperatures of 60 to 90° C. Boron hydride hydrazine ($N_2H_4BH_3$) is more promising. It dissolves readily in water and is not easily hydrolyzed. The pH of a boron hydride hydrazine solution is 7.5 at room temperature. The reduction reaction with nickel is as follows:[4]

$$3Ni^{2+} + N_2H{\cdot}BH_3 + 3H_2O \rightarrow 3Ni + N_2H_4 + H_3BO_3 + 6H^+ \quad (1)$$

A side reaction that can occur is:

$$3Ni^{2+} + 2(N_2H_4{\cdot}BH_3) \rightarrow \quad (2)$$

$$3H_2O + Ni_3B + 2N_2H_4 + 6H^+ + H_3BO_3 + 3/2H_2$$

The nickel deposit is not harmfully affected by the oxidation products of borohydrazine—hydrazine and boric acid—nor do the products affect the rate of deposition. Improved physical properties have been obtained with the incorporation of 3 to 5 percent boron in the deposit.[1]

Experimental Procedure

ABS plastic specimens were cleaned for 5 min in a 50° C solution containing 40 g/L of sodium carbonate and 20 g/L of trisodium phosphate, then rinsed with hot (60° C) water for 5 min. Surfaces were etched (10 to 20 min) in a 360-g/L chromic acid bath containing 150 mL/L of concentrated sulfuric acid, which was heated to 60-65° C. After rinsing, a 300-mL/L solution of hydrochloric acid was used at temperatures up to 50° C for 2 to 5 min for neutralization purposes. Samples were rinsed first in tap water, then distilled water before sensitization (10 to 15 min) in a solution at room temperature prepared with 20 g/L of $SnCl_2{\cdot}H_2O$ and 100 mL/L of concentrated hydrochloric acid. This was followed by distilled water and tap water rinses. A subsequent activation treatment in a 20 to 40° C solution prepared with 0.25 g/L of $PdCl_2$ and 2.5 mL/L of concentrated HCl was continued for 10 to 15 min. After rinsing, first in tap water, then distilled water, samples were immersed in the electroless nickel bath for 30 min.

The nickel bath was prepared with 75 g/L of $NiCl_2{\cdot}6H_2O$, 1 to 1.5 g/L of $N_2H_4{\cdot}BH_3$, 20 g/L of CH_3COONa and 0.1 mmol/L of $Na_2S_2O_3$. The pH of the bath was 7.5, the deposition time was 30 min and the load density was in the range of 1 to 2 dm^2/L.

Boron hydride hydrazine was synthesized by the method reported by Gabeau and Ricker,[5] which involved the following exchange reaction:

$$2NaBH_4 + (N_2H_5)_2SO_4 \xrightarrow{30-35^\circ C} 2N_2H_4{\cdot}BH_3 + Na_2SO_4 + 2H_2 \quad (3)$$

The rate of deposition, the quality of the coatings and the bath efficiency were examined while changes were made in the composition of the bath. The bath efficiency was determined by calculating the ratio of the weight of the nickel deposit and the decrease of nickel ions in the solution, which was determined by chemical analysis using titration with versenate.

Results

Figures 1 and 2 show the effects of increasing the boron hydride hydrazine concentration on the deposition rate and the bath efficiency, respectively. Increasing the concentration of the reducing agent above 1.5 g/L did not significantly improve the deposition rate. For obtaining a high efficiency and a high deposition rate, a reducing agent concentration of 1.0 to 1.5 g/L appeared optimum. The effect of changing the concentration of sodium boron hydride hydrazine on the pH of the solution is shown in Fig.3.

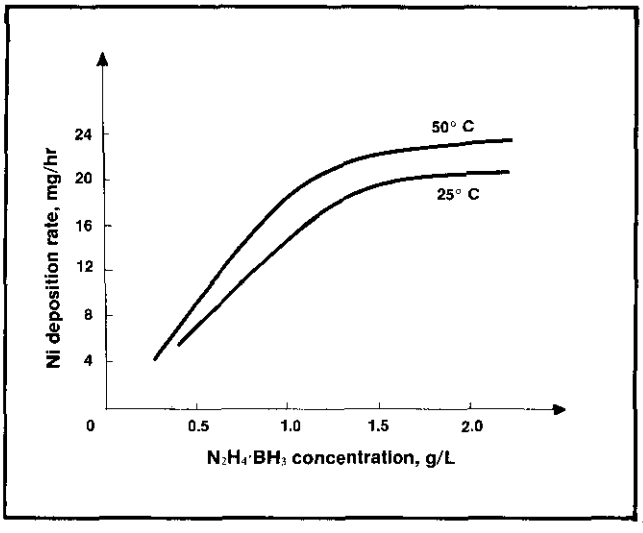

Fig. 1—Nickel deposition rate as a function of the initial concentration of boron hydride hydrazine.

control and uniformity are necessary. During a series of cross-sectional TEM observations, a linear relationship between film thickness and deposition time was recorded (Fig. 9). Film thickness was measured with high resolution and precision directly from TEM micrographs. Figure 10 shows a typical TEM micrograph of a 300-Å-thick cross section of a Fe-Ni alloy deposit on a (111) n-type silicon substrate. The sharp interface between the substrate and Fe-Ni deposit indicates that it might be possible to fabricate shallow junction boxes after a suitable annealing schedule.

Lateral growth is considered to be the dominant mechanism of film growth until full coverage is obtained and thicker films are formed. On the other hand, deposition rates differed on different kinds of Si even when operating conditions were unchanged. For example, the rate on n/n^+-Si differed from that on n-Si. The immediate deposition of Fe-Ni alloy on semiconductor Si without conventional sensitizing or activating steps is probably a result of the excess donor electrons of n-type Si that are available in sufficient quantity to start the reduction process. Thus, the process that includes Si etching provides a clean surface that is not contaminated with Sn or Pd and a means of fabricating silicide/Si Schottky diodes via thermal annealing programs.[11,12] The mechanism of film formation and growth described in this paper can ultimately help to form new materials and devices with properties required for practical applications.

Conclusions

Iron-nickel alloy has been deposited on n-type Si single crystals using electroless deposition in a solution containing hydrazine. EDAX linked with TEM showed that the alloy contained 88 atomic percent iron and 12 atomic percent nickel. The structure is amorphous. Film formation is completed in about 8 min and the deposition rate is about 50 Å/min. A sharp interface was observed between the Fe-Ni deposit and the Si interface.

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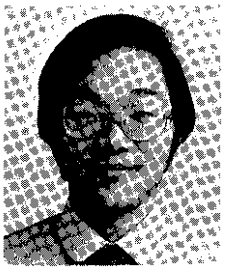

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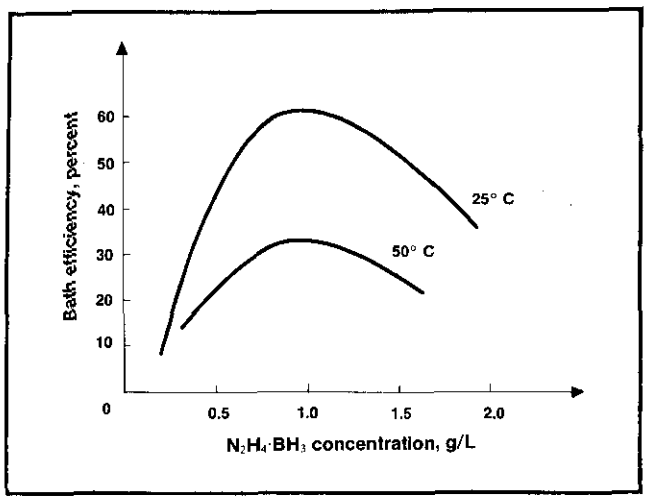

Fig. 2—Effect of boron hydride hydrazine concentration on bath efficiency.

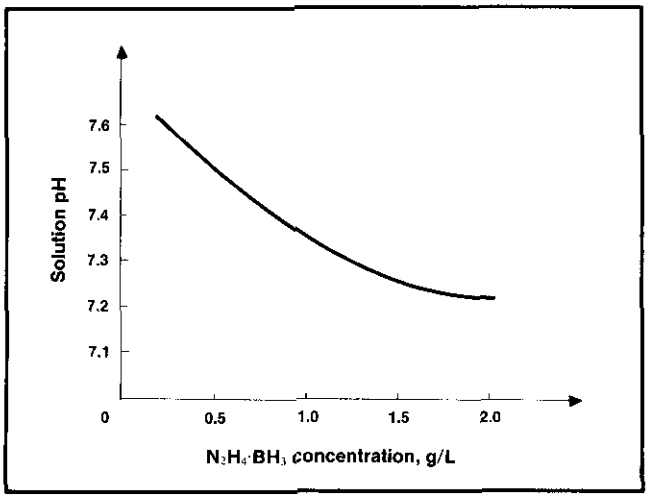

Fig. 3—Effect of the initial concentration of boron hydride hydrazine on the pH of the electroless solution at 25° C.

A high rate of deposition and a high efficiency were obtained when the bath contained 15 to 17 g/L of nickel ions, as shown in Figs. 4 and 5, respectively. Figure 6 data also indicate that consumption of the reducing agent was low when the nickel ion concentration was in this 15 to 17 g/L range. An increase above 17 g/L did not improve the deposition rate. However, efficiency declined significantly (Fig. 5) and consumption of boron hydride hydrazine increased.

Substituting nickel sulfate for nickel chloride reduced the deposition rate and increased consumption of the reducing agent, although no other differences in performance were observed.

A sodium acetate concentration above 20 g/L caused dark and sometimes spotted deposits. Figure 7 shows that the deposition rate was maximum at a concentration of 20 g/L and decreased significantly when the acetate concentration was lower or higher.

In preliminary tests, ethylene diamine was rejected as a stabilizing agent because it raised the solution pH to 10.5. Previous papers[1-6] indicated that better results were obtained on plastics metallized in solutions with a lower pH. Sodium thiosulfate proved to prevent the precipitation of nickel in the bulk solution. However, increasing its concentration to >0.075 mmole/L increased consumption of the reducing agent, relative to the amount of nickel deposited, and resulted in dull, dark coatings, which were particularly pronounced when the temperature ranged from 20 to 30° C (Figs. 9 and 10). The nickel:reducer ratio was less than 1.5 by using the bath containing sodium thiosulfate, as Fig. 10 shows.

The relationship between nickel deposition rate and load density is shown in Fig. 11. Figure 12 shows the effect of changing load density on nickel consumption. The nickel deposition rate as a function of temperature appears in Fig. 13, and the influence of the initial pH on the deposition rate is shown in Fig. 14. From the data in Figs. 11-14, the optimum load density, temperature and pH were determined:

Optimum load density: 1.5 g/L
Optimum temperature: 30 to 35° C
pH: 6.6 to 7.6

Although temperatures above 35° C improved the deposition rate (Fig. 13), the higher temperatures caused greater consumption of the stabilizing and reducing agents. The average bath efficiency at 30° C was 57.5 percent, which compares with an efficiency of 54 to 55 percent for operating a bath with sodium hypophosphite as the reducing agent.

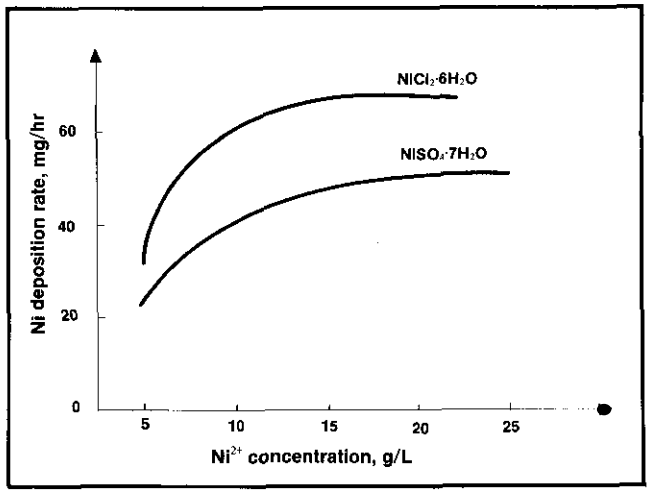

Fig. 4—Nickel deposition rate as a function of nickel ion concentration in a bath at 30° C.

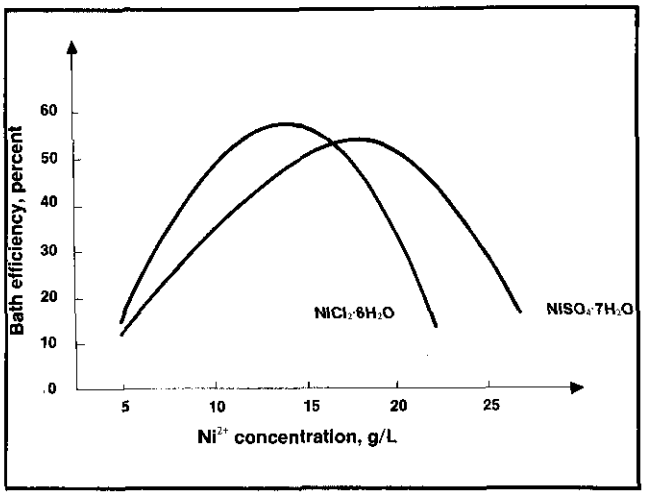

Fig. 5—Nickel deposition efficiency as a function of nickel ion concentration.

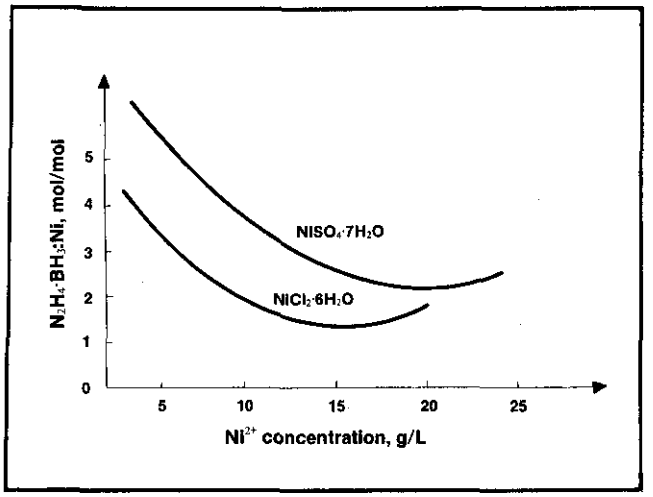

Fig. 6—Relationship between the concentration of Ni^{2+} and the ratio of boron hydride hydrazine consumption to the amount of deposited nickel.

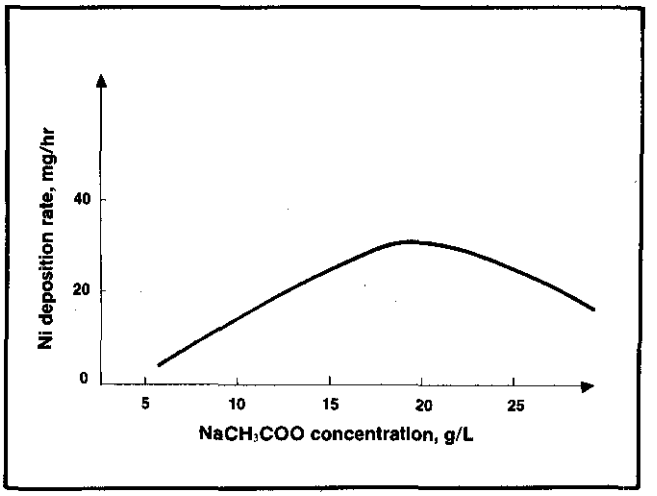

Fig. 7—Nickel deposition rate at 30° C as a function of sodium acetate concentration.

The pH tends to rise during bath operation, as reducing agent is consumed. This increase is associated with the formation of hydrazine and boric acid, according to equations (1) and (2). To compensate for the reduction in the concentration of nickel ions and boron hydride hydrazine, the concentration of nickel was corrected, after a titration with versenate. The pH was then adjusted to 7.5 using sodium hydroxide. The concentration of boron hydride hydrazine was determined by an iodometric titration of BH_3 in an acid solution as described previously.[7] Finally, the concentration of the reducing agent was adjusted. When adjustments were made several times during a single experiment, changes in the quality of the coatings were not observed. The deposits were semibright and adherent. Thickness ranged from 2 to 6 μm.

After nickel and chromium were plated on the electroless nickel, the bond between the metal and plastic surfaces was examined by subjecting samples to thermal cycle tests. The procedure described in ASTM B-553 with a high limit of 60° C for 1 hr and a low limit of -30° C for 1 hr was adopted. The cycle was repeated five times. The percentage of samples with no blisters was 91 percent.

Microscopic examination of electroless deposits revealed many pores with a diameter of 1 to 2 μm.

Conclusions

A nearly neutral, low-temperature bath using boron hydride hydrazine as the reducing agent proved useful for depositing adherent, electroless nickel on etched, sensitized and accelerated ABS. The average efficiency of the electroless bath operated with optimum conditions was 57.5 percent. No deterioration in the quality of the deposits occurred when nickel chloride and boron hydride hydrazine were replenished and the pH adjusted as described in this paper. The bath can be adjusted and reused many times.

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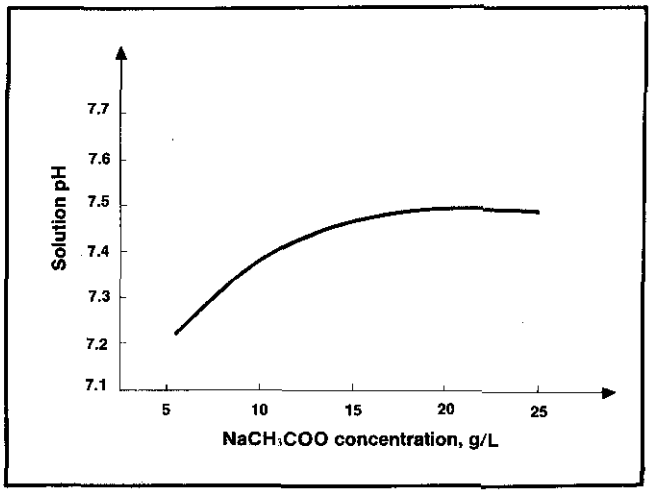


Fig. 8—Influence of sodium acetate concentration on pH of the solution.

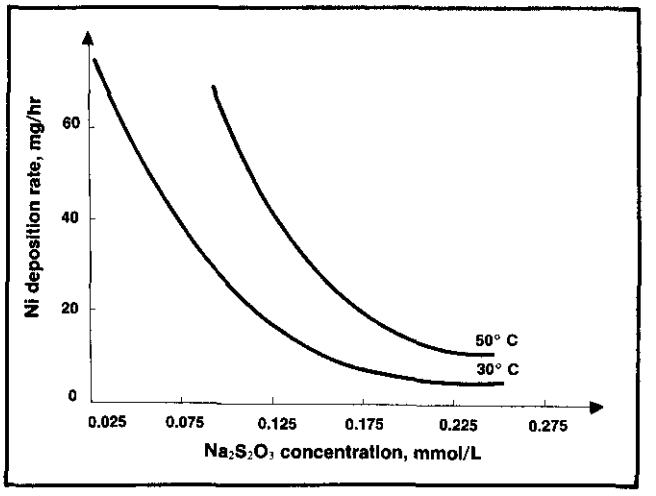


Fig. 9—Nickel deposition rate as a function of the concentration of sodium thiosulfate.

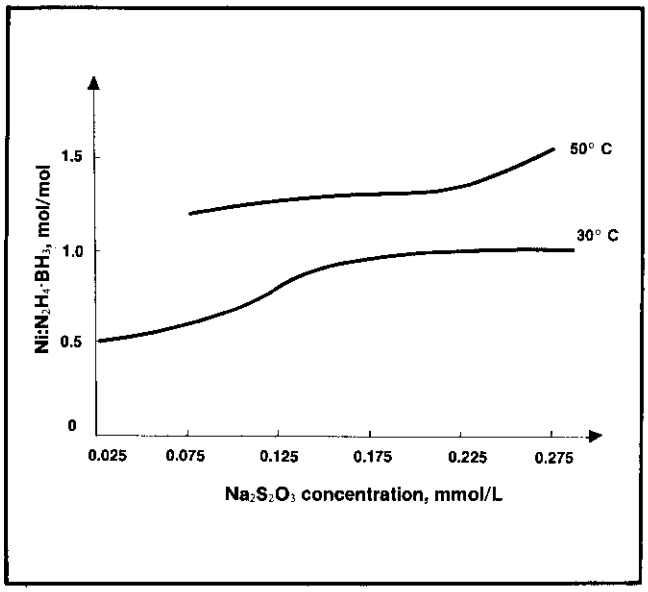


Fig. 10—Relationship between sodium thiosulfate concentration and the ratio of reduced nickel to consumed $N_2H_4 \cdot BH_3$.

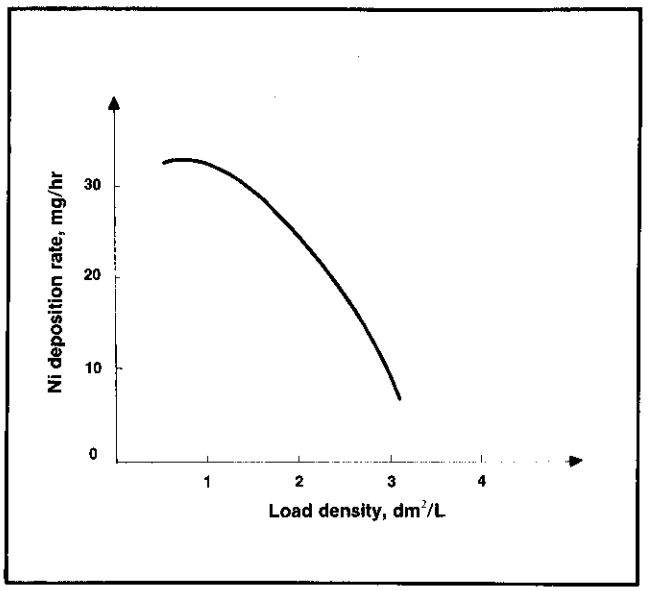


Fig. 11—Nickel deposition rate at 35° C as a function of load density.

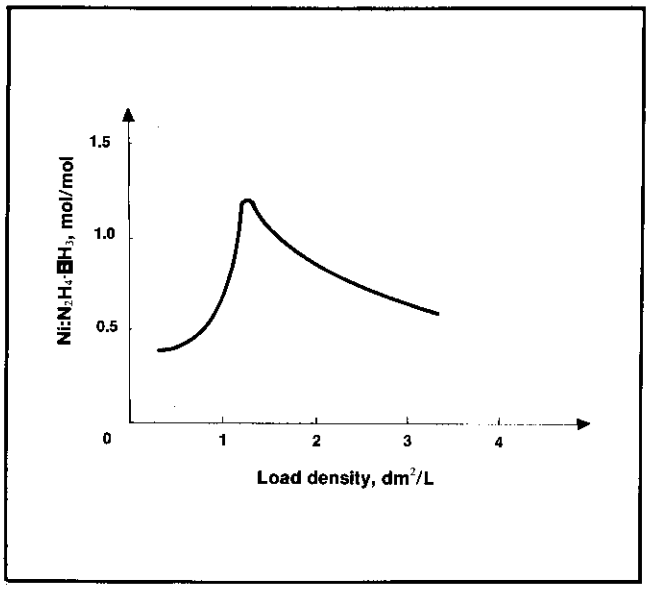


Fig. 12—Relationship between load density and ratio of reduced nickel to consumed $N_2H_4 \cdot BH_3$.

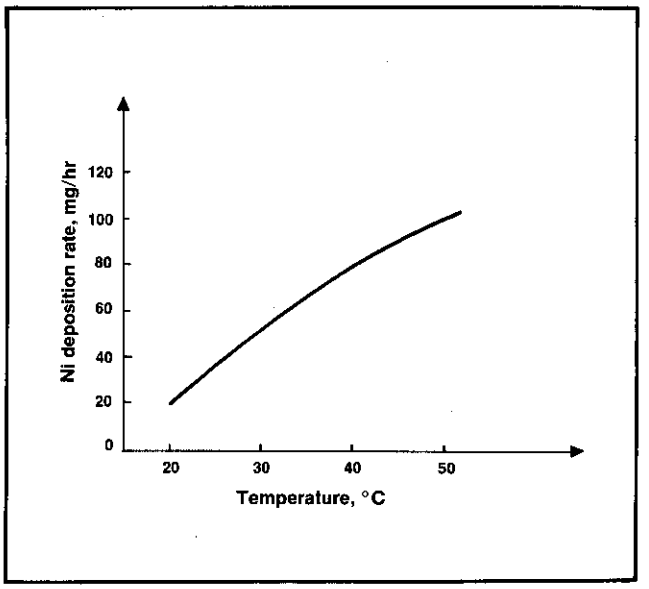


Fig. 13—Nickel deposition rate as a function of temperature.

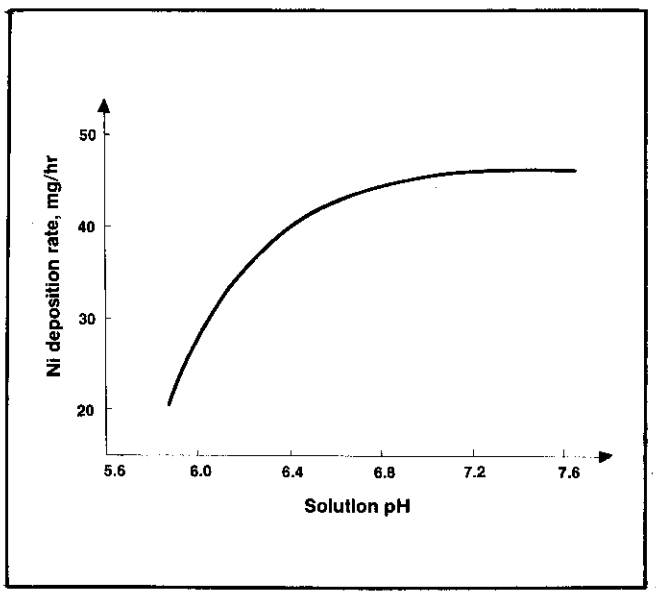
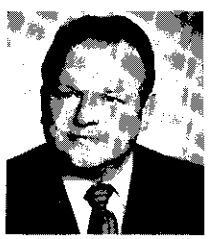


Fig. 14—Nickel deposition rate as a function of initial solution pH.



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